
III.D.4 Determination of Electrochemical Performance and Thermo-Mechanical-Chemical Stability of SOFCs from Defect Modeling

Objectives

- Advance the fundamental understanding of the continuum-level electrochemistry of oxide mixed ionic-electronic conductors (MIECs) in relation to their performance in SOFCs.
- Obtain fundamental constants required for implementing the continuum-level electrochemical model from experiment.
- Extend the models to multilayer structures and incorporate microstructural effects.
- Verify the models through experiment.
- Develop a transient version of the continuum-level electrochemical model.
- Obtain time constants for various transport processes from electrical impedance spectroscopy to examine the effects of transients on SOFC performance.
- Develop and deliver software modules for incorporation of the continuum-level electrochemical model into SOFC failure analysis software used by National Energy Technology Laboratory, Pacific Northwest National Laboratory, Oak Ridge National Laboratory, and the SECA industrial teams.

Accomplishments

- Completed a continuum-level electrochemical model (CLEM) for *steady state* conditions, using potential dependent boundary conditions and non-linear Galvani potential.
- Completed a CLEM for *transient* conditions, using potential dependent boundary conditions and a linear Galvani potential.
- Compiled software modules for vacancy concentration and electron concentration in *n*-type and *p*-type MIECs.

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- Extended the CLEM to thermo-mechanical and thermo-chemical properties of MIECs.
- Extended the CLEM to YSZ/LSM (YSZ/lanthanum strontium manganate) and YSZ/LSCF (YSZ/lanthanum strontium cobalt ferrite) bilayers.
- Measured the thermal expansion of ceria and acceptor-doped ceria in air and reducing atmospheres. Results concur with model predictions.
- Obtained time constant for equilibration of material after a change in P_{O_2} during chemical expansion.
- Measured the elastic moduli of ceria, gadolinia-doped ceria (GDC) and YSZ in reducing (H_2) and oxidizing atmospheres (air) using nondestructive and (nanoscale) destructive techniques; both showed that reducing conditions cause a ~30% decrease in the elastic modulus relative to air. Results concur with model predictions.
- Evaluated polycrystalline elastic modulus of ceria after heat treatment in air and in hydrogen using 4-point bending test—results are consistent with nanoindentation results and model.
- Measured the fracture toughness of ceria and GDC in reducing (H_2) and oxidizing atmospheres (air); results show that reducing conditions cause a ~37% increase in the fracture toughness relative to air.
- Deconvoluted transport processes for optimally sintered LSM and LSCF, with time constants ranging from 10^{-10} (charge transfer) to 10^5 seconds (gas diffusion).
- Established a relationship between electrochemical and microstructural properties: dissociative adsorption polarization resistance increases as pore surface area decreases and charge transfer polarization resistance increases as triple phase boundary length increases.

Introduction

For extensive deployment of SOFCs into industrial and consumer markets to become a reality, some key hurdles need to be cleared. Three of these hurdles are (i) mechanical, (ii) chemical and (iii) transient stability of SOFCs. In our research we are tackling these hurdles by developing models to relate point defect population distribution and microstructure to the electrochemical and mechanical properties of SOFC components, which are then the actual determinants of the thermo-mechanical, thermo-chemical and transient stability of

SOFCs. These fundamental-level models can then be incorporated into system-level models to predict and analyze SOFC performance and response to various inputs.

Approach

To develop models for the relationship between point defect population distribution and microstructure to the electrochemical and mechanical properties of SOFC components, first we modeled the generation of point defects in oxide MIECs as a function of atmosphere (P_{O_2}) and temperature. Next we modeled the transport and distribution of defects in an MIEC in a P_{O_2} gradient, by solving the Nernst-Planck, mass conservation and charge conservation equations for Laplacian and non-Laplacian potential distributions. These two steps produced a CLEM that relates point defect concentration to operating conditions and material properties. Hence, by modeling or applying relationships between point defects and indices for thermo-mechanical, thermo-chemical and transient stability, secondary relationships between these indices and the SOFC operating conditions and material properties can be derived. Finally, experiments have been conducted to confirm the predictions of the models as well as to give more insight into the factors and mechanisms that play a role in the performance of the SOFC components and the overall stability of the SOFC.

Results

CLEM–Defect Thermodynamics. To obtain defect concentration dependence on P_{O_2} , equations that are continuous across at least two regimes were derived [1]. Excellent results were obtained when these equations were fitted to experimental data [1]. The ability to predict defect concentration as a function of P_{O_2} then allows us to model various MIEC properties that depend on P_{O_2} such as conductivity, chemical expansion and elastic modulus.

CLEM–Defect Transport. To model defect transport in MIECs we solved the Nernst-Planck, material balance, and current density equations with *potential-dependent* boundary conditions and without assuming a linear, i.e., Laplacian, potential distribution [2]. Our results predict the transport properties of the MIEC components and SOFC performance. Assuming a linear potential ignores the efficiency sapping effects of mixed conduction and using *fixed* boundary conditions lessens the effects of concentration gradients; together they lead to overestimation of cell performance.

Figure 1 shows a comparison of our results compared with that of Kim *et al* [3] for modeling the current-voltage (I-V) characteristics of a Ni-YSZ/YSZ/LSM cell. We modeled cell performance with similar

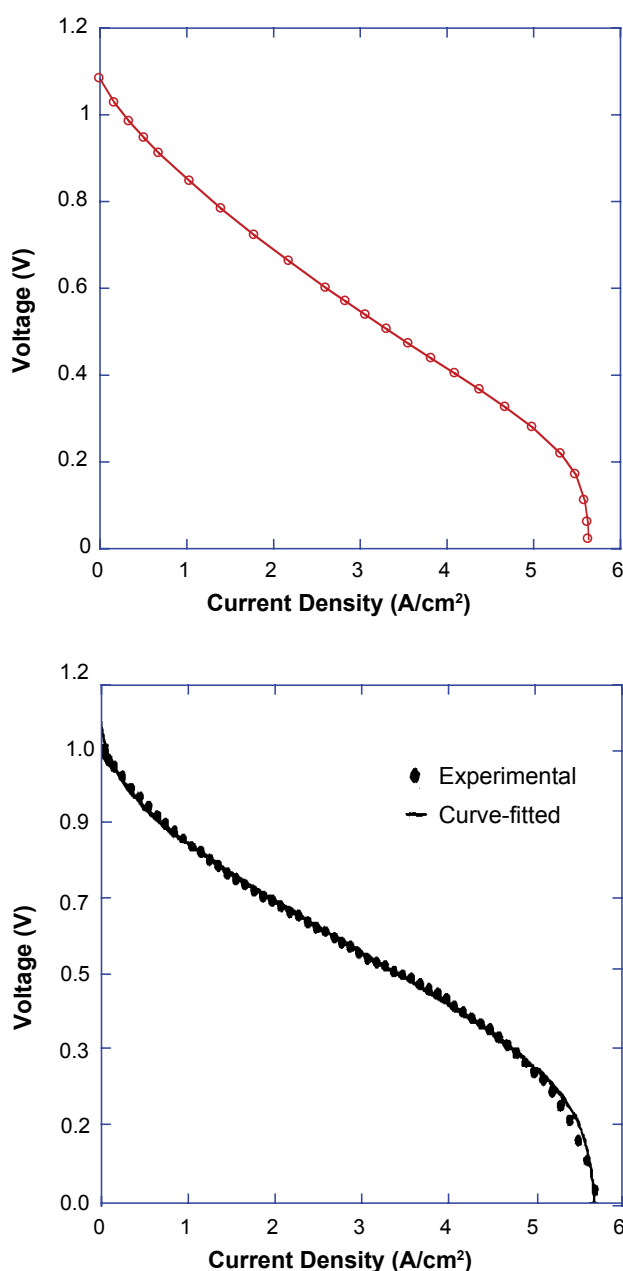


FIGURE 1. Comparison of Theoretical Models Fit to Experimental Data (top); Present Work (bottom) Kim *et al* [3]

accuracy to Kim *et al*. However, less fitting parameters (3 vs. 10) were used in our model. Moreover, because our model does not assume a uniform vacancy concentration, it is amenable for modeling cells with alternative electrolytes, e.g., GDC.

CLEM–Chemical Expansion. To extend the CLEM to chemical expansion of MIECs, a relationship for chemical expansion was derived, as follows

$$\frac{\Delta l}{l_0} = \alpha \Delta T + \frac{\beta}{a_0} c_V \quad (1)$$

where T is temperature, $\Delta l/l_0$ is expansion and β is a material constant related to lattice structure. This allows us to predict the chemical expansion of various SOFC components and associated stresses caused by mismatches between components or P_{O_2} gradients. Figure 2a shows an excellent fit between model and experimental data and that there is significant chemical expansion in ceria and GDC, which correlates to the onset of mixed conduction [1].

CLEM–Mechanical Properties. To extend the CLEM to mechanical properties of MIECs, a relationship between defect population and elastic modulus, E , was derived by considering that the bond energy, U , between atoms in a crystal, may be

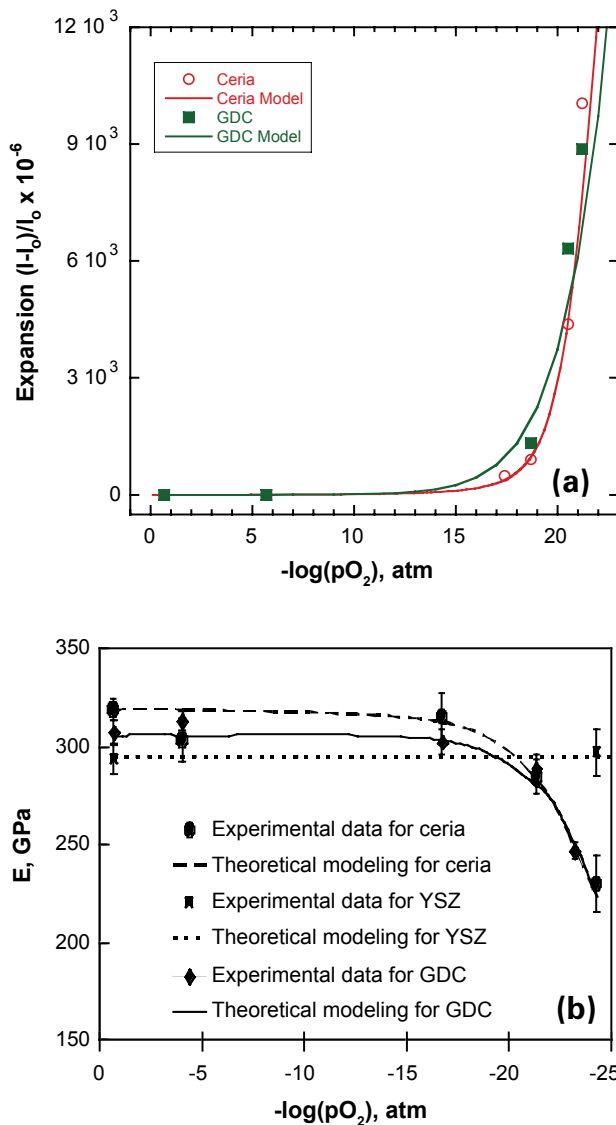


FIGURE 2. Data and model fit for (a) Chemical expansion of ceria and GDC at 1073 K (b) Elastic moduli of ceria, GDC and YSZ as a function of P_{O_2} .

approximated by $U = A/r^n - B/r^m$; where r is the inter-atomic distance, and A , B , n and m are empirically determined constants [4]. Thus, the elastic modulus for a perfect crystal, $E \approx 1/r_0(d^2U/dr^2)_{r=r_0}$ [4]; or

$$E(x) \approx E^* (\theta c_v(x) + 1)^{-(n+3)} \quad (2)$$

where c_v is vacancy concentration, θ is an empirically determined constant, and E^* is the stoichiometric elastic modulus.

Using a triboindenter, we measured the elastic modulus of individual grains of ceria, GDC and YSZ samples annealed in a range of P_{O_2} 's between air and H_2 . The results, Figure 2b, show good fits of the model to experiment. Therefore, we can predict how the mechanical properties of SOFC components will change as a function of P_{O_2} .

Comparisons of the elastic modulus for polycrystalline samples with nanoindentation results (intrinsic elastic modulus) for both ceria and YSZ are shown in Figure 3. Although the samples experienced the same thermo-chemical treatment, a lower modulus

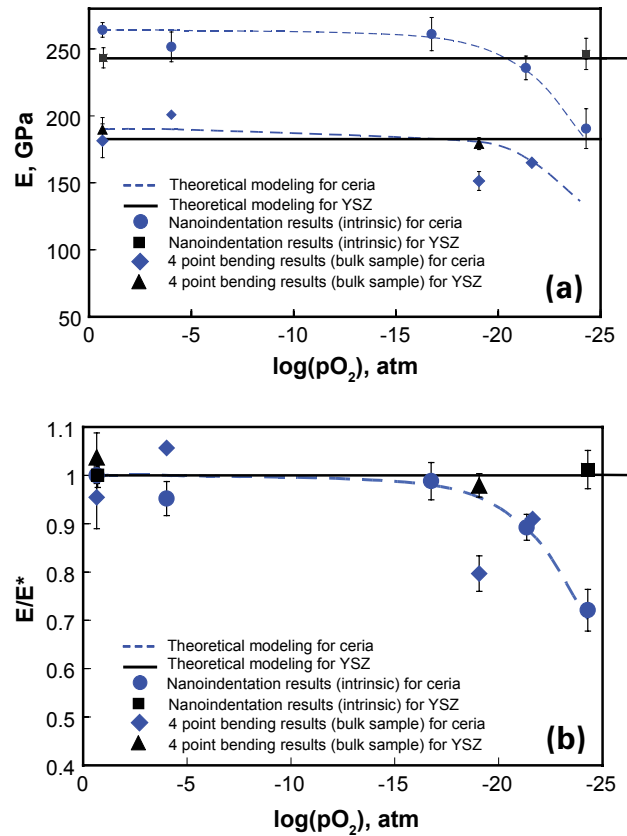


FIGURE 3. Comparison of the intrinsic elastic modulus (from nanoindentation) and polycrystalline elastic modulus (from 4-point bending) of ceria and YSZ (a) elastic modulus as a function of P_{O_2} (b) the relative change of elastic modulus as a function of P_{O_2} .

was obtained from the 4-point bend test compared to the intrinsic modulus. The reasons for this observed difference stem from the different nature of the experiments as well as the effects of pores/microcracks in the polycrystalline sample, which were caused by processing and heat treatment.

More importantly, however, Figure 3b shows that the relative change in elastic modulus as a function of P_{O_2} , obtained from either test is the same and is exactly predicted by the model. This is an emphatic validation of the model's correctness and indicates that oxygen vacancies play an important role in the thermo-mechanical properties of polycrystalline ceramics.

The effects of lattice vacancy concentration on fracture toughness (K_{IC}) of ceria were measured using Brazilian disc samples loaded under mode I conditions [5]. Fracture toughness test results are shown in Table 1. The sample heat treated in air has a room temperature K_{IC} value of $0.96 \text{ MPa}\cdot\text{m}^{1/2}$. Surprisingly, K_{IC} increased as much as 30-40% for the samples heat treated under reducing conditions.

TABLE 1. Fracture Toughness (K_{IC}) of Ceria

Heat Treatment	# of Samples Tested	P_{O_2} , atm.	K_{IC} , $\text{MPa}\cdot\text{m}^{1/2}$
H_2	2	4.5×10^{-22}	1.32 ± 0.04
H_2/H_2O	2	1.5×10^{-20}	1.40 ± 0.01
N_2	1	4.5×10^{-6}	0.92
Air	3	0.21	0.96 ± 0.05
As-sintered	1	-----	0.91

Fracture toughness can also be expressed in terms of the critical elastic energy release rate, G_c , as: $K_{IC} = \sqrt{(G_c E)}$. In brittle materials, G_c is proportional to the energy released in creating new surfaces. Since elastic modulus, E , decreases with decreasing P_{O_2} , this indicates that exposure to low P_{O_2} increases G_c and that there is some relationship between G_c and oxygen vacancy concentration.

To understand the higher toughness values for the samples heat treated in P_{O_2} 's, the fracture surface was studied using scanning electron microscopy (SEM), which revealed that the sample heat treated in air has a relatively smooth fracture surface, but the sample has a notably rougher fracture surface when heat treated in H_2 , which is consistent with the higher K_{IC} value. Possible factors for the rough fracture surface are, pore-crack interactions, microcrack formation, internal stresses and phase transformation.

We have identified the primary contributions to the impedance of LSM cathodes on YSZ electrolyte substrates for conventional SOFCs. The processes

and their related time constants are shown in Figure 4 and Table 2. This now enables cathode developers to correctly assess how changes in cathode parameters [e.g., triple-phase boundary (TPB), porosity, etc.] affect each transport process. Moreover, knowing the time constant for each process helps in predicting SOFC response in transient conditions.

Chemical-Stability. The CLEM was applied to the chemical stability of LSM/YSZ and LSCF/YSZ interfaces, including electrode microstructure. The results provide the P_{O_2} at the interface, and thereby the

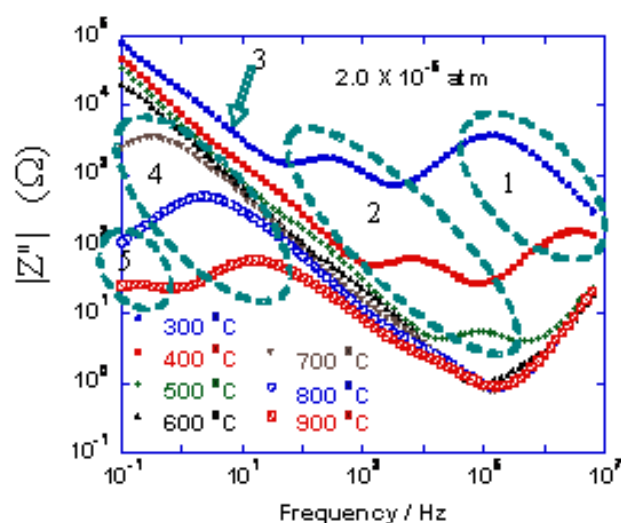


FIGURE 4. Deconvolution of LSM/YSZ/LSM symmetric cell impedance from AC-Impedance Spectroscopy. The transport process corresponding to each number is given in Table 2.

TABLE 2. Deconvolution of AC-Impedance Spectra for LSM/YSZ/LSM Symmetrical Cells

Process	"m" in $\log R \propto m \log P_{O_2}$	Activation energy, E_a (eV)	Time constant, τ (s) @ 800°C
1. Ionic diffusion through electrolyte bulk	0.0084	1.10	
2. Ionic diffusion across electrolyte grain boundary	-0.022	1.04	
3. Charge transfer of O^{2-} from TPB into YSZ	-0.046	0.97	8.5×10^{-5}
4. O_2 dissociation and surface diffusion on LSM	-0.15	1.2	0.18
5. Gas diffusion through porous electrode	-1.1	~ 0.04	5.9

interfacial stability, as a function of operating conditions (more detail may be obtained from previous reports).

Transient Response. The CLEM has been extended to transient conditions (more detail may be obtained from previous reports). To obtain solutions, we assumed a linear potential distribution. This assumption is best applied to predominantly ionic conductors, e.g., YSZ or predominantly electronic conductors, e.g., LSM.

Software Development. The development of software modules for the CLEM is in progress. At this point, the program for the *steady-state* CLEM for defect generation and transport has been completed. Two languages were used, C++, because it is the industry standard, and PHP, because of its web oriented features.

Conclusions and Future Directions

- A continuum-level electrochemical model has been developed that improves on preceding efforts by including a non-linear potential distribution and by including potential dependent boundary conditions.
- The continuum-level electrochemical model has been extended to describe thermo-mechanical, thermo-chemical and transient stability in MIECs.
- Experimental results concur with the predictions of the continuum-level electrochemical model for electrical conductivity.
- Nanoindentation (intrinsic) tests on ceria, GDC and YSZ with different level of oxygen concentration revealed that the elastic modulus of ceria and GDC decreases considerably as the oxygen lattice vacancy concentration increases. The elastic modulus of YSZ within the studied P_{O_2} and temperature range was insignificantly changed due to the small number of lattice vacancy produced. GDC and ceria showed very similar trends.
- Four-point bend (polycrystalline) tests on ceria, GDC and YSZ with different levels of oxygen concentration revealed that the elastic modulus of ceria and GDC decreases considerably as the oxygen lattice vacancy concentration increases and the elastic modulus of YSZ within the studied P_{O_2} and temperature range was insignificantly changed due to the small number of lattice vacancy produced.
- The P_{O_2} dependence obtained from nanoindentation (intrinsic) and 4-point bend (polycrystalline) tests are both consistent with each other and the model. This indicates that oxygen vacancies play an important role in the thermo-mechanical properties of polycrystalline ceramics.
- In order to separate the effects of oxygen vacancies on K_{IC} , future work on high temperature microstructure/fracture surface analysis and molecular dynamic simulations is needed.
- The continuum-level electrochemical model has been validated through experiment for thermo-mechanical properties (elastic modulus and thermo-chemical expansion).
- The *steady-state* version of the continuum-level electrochemical model has been written in C++ and PHP.

FY 2006 Publications/Presentations

1. Y. Wang, K. Duncan, E. Wachsman, F. Ebrahimi, *Solid State Ionics*, submitted.
2. K. L. Duncan, Y. Wang, S. R. Bishop, F. Ebrahimi and E. D. Wachsman, *J. Amer. Ceramics Soc.*, (2006) accepted.
3. E. D. Wachsman, "Fundamental Studies of SOFC Materials," *DOE - SECA Core Technology Program Peer Review Meeting*, Denver, CO, October 25-26, 2005.
4. Y. Wang, K. Duncan, E. Wachsman and F. Ebrahimi, "Effects of Oxygen Vacancy Concentration on Mechanical Properties of Cerium Oxide", *ECS Transactions Solid State Ionic Devices IV*, (2005).
5. S. R. Bishop, K. L. Duncan, E. D. Wachsman, "Chemical Expansion of SOFC Materials" *The 208th ECS meeting, The Electrochemical Society*, Los Angeles, CA, October 2005.
6. S. R. Bishop, K. L. Duncan, E. D. Wachsman, "Chemical Expansion of SOFC Materials" *The 30th International Conference on Advanced Ceramics and Composites. The American Ceramics Society*, Cocoa Beach, FL, January 2006.
7. J. R. Smith, A. Chen, D. Gostovic, D. Hickey, D. P. Kudinger, K. L. Duncan, K. Jones, and E. D. Wachsman, "The Relationship Between Cathode Microstructure and Electrochemical Behavior for SOFCs", *30th International Conference & Exhibition on Advanced Ceramics & Composites*, Cocoa Beach, FL, January 2006.
8. J. R. Smith, K. L. Duncan, M. E. Orazem, and E. D. Wachsman, "Evaluation of Time Constants Governing the Cathodic Reaction in SOFCs", *208th Meeting of the Electrochemical Society*, Los Angeles, CA, October 2005.

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